

HEAT-RESISTANT MAGNESIUM ALLOY FOR CASTING

AND

HEAT-RESISTANT MAGNESIUM ALLOY CAST PRODUCT

BACKGROUND OF THE INVENTION

Field of the Invention

**【0001】** The present invention relates to a heat-resistant magnesium alloy which can inhibit cracks when being cast, and which is good in terms of the castability and heat resistance.

Description of the Related Art

**【0002】** Due to the recent increasing weight reduction need, magnesium alloys which are much lighter than aluminum alloys have been attracting the attention of engineers. Magnesium alloys are the most lightweight among practical metals, and are about to be used as automotive materials in addition to aeronautical materials. For example, magnesium alloys are used in automobile wheels and engine head covers. In addition to these, as the environmental consciousness has been enhanced recently, it has been required to further make vehicles lightweight. Accordingly, it has come to examine to use magnesium alloys even for appliances or apparatuses which are used in high-temperature regions. In this instance, the heat resistance of magnesium alloys matters naturally. For instance, AZ91 as per Japanese Industrial Standard, a general magnesium alloy, exhibits such a very low creep strength that it is not appropriate for component parts which are used in high temperature environments. Consequently, AE42 as per the standard of the Dow Chemical Company of the United States of America is available as one of such materials whose heat resistance is improved. Moreover, Japanese Patent Publication No. 3,229,954, Japanese

Unexamined Patent Publication (KOKAI) No. 2002-129,272 and Japanese Unexamined Patent Publication (KOKAI) No. 2002-275,569 propose magnesium alloys which are good in terms of the anti-creep strength or the other properties.

**[0003]** All of these magnesium alloys include rare-earth elements (hereinafter abbreviated to as "R.E." wherever appropriate) in an amount of from 0.5 to 3% by mass approximately. Rare-earth elements are surely effective elements in improving the heat resistance of magnesium alloys.

**[0004]** However, rare-earth elements are so expensive that they raise the cost of magnesium alloys and their cast products. Moreover, according to the survey and study carried out by the present inventors, rare-earth elements are found to be elements which are likely to cause cracks in casting alloys. Accordingly, it is not preferable to have rare-earth elements contained in cast alloys. In addition, the present inventors have come to know newly that it is possible to produce heat resistance, such as sufficient creep resistance, without including rare-earth elements in magnesium alloys.

#### SUMMARY OF THE INVENTION

**[0005]** The present invention has been developed in view of such circumstances. It is therefore an object of the present invention to provide a heat-resistant magnesium alloy for casting, magnesium alloy which can inhibit the occurrence of cracks when being cast, and which is good in terms of the castability, not to mention the heat resistance, without using rare-earth elements but by using elements being less expensive than rare-earth elements. Moreover, it is a further object of the present invention to simultaneously

provide a magnesium alloy cast product which is cast by using the aluminum alloy.

**[0006]** Hence, the inventors of the present invention studied wholeheartedly in order to solve the problem, and carried out a variety of systematic experiments repeatedly. As a result, when only Al and Ca, which are less expensive fundamentally, are contained in magnesium alloys in an appropriate amount, respectively, they found out that it is possible to produce magnesium alloys which exhibit sufficient heat resistance and simultaneously which is good in terms of the castability so that cracks are less likely to occur in casting. Based on the discovery, they arrived at completing the present invention.

(Heat-resistant Magnesium Alloy for Casting)

**[0007]** For example, a heat-resistant alloy according to the present invention is for casting, is good in terms of the castability and heat resistance, and comprises:

calcium (Ca) in an amount of from 1 to 15% by mass;  
aluminum (Al) in a summed amount of from 4 to 25% by mass with the amount of Ca; and

the balance being magnesium (Mg) and inevitable impurities when the entirety is taken as 100% by mass (hereinafter simply referred to as "%").

**[0008]** The present heat-resistant magnesium alloy does not contain expensive "R.E." Moreover, since the requisite elements of the present heat-resistant magnesium alloy are only Ca and Al, the present heat-resistant magnesium alloy and heat-resistant magnesium alloy cast products made of the same are less expensive and are remarkably good in terms of the cost competitiveness even

when not only the material cost and but also the production cost are taken into consideration. In addition, the present heat-resistant magnesium alloy not only demonstrates sufficient heat resistance but also effects an advantage that cracks are inhibited from occurring in casting as described above.

**【0009】** Incidentally, it is not necessarily clear why the present heat-resistant magnesium alloy exhibits good heat resistance and castability when it contains only Ca and Al in an amount falling in the aforementioned range, respectively. However, it is believed at present as hereinafter described.

**【0010】** First, the reasons why the present heat-resistant magnesium alloy is good in terms of the heat resistance will be hereinafter described.

**【0011】** Al is an important element in view of improving the room-temperature strength of magnesium alloys when it solves in magnesium crystalline grains. Moreover, Al is an important element in view of upgrading the corrosion resistance of magnesium alloys. However, when the Al content increases in magnesium alloys, Al solves in the matrices of magnesium alloys, such as dendritic cells and  $\alpha$  crystalline grains, supersaturatedly to form Al-rich phases. Since the Al-rich phases are unstable thermally, they turn into Mg-Al compounds, such as  $Mg_{17}Al_{12}$ , to precipitate in the magnesium matrix or magnesium crystalline grain boundaries when magnesium alloys are heated to high temperatures. When such magnesium alloys are left in a high-temperature region for a long period of time, the intermetallic compounds agglomerate to such coarsened grains that the creep deformation of magnesium alloys is enlarged. That is, the heat resistance of magnesium alloys is lowered.

**【0012】** Ca produces an effect of inhibiting the heat-resistance decrement accompanied by the Al content increment. This is believed to result from the fact that Ca reacts with the Mg-Al compounds and matrices to decrease  $Mg_{17}Al_{12}$ , which causes to lower creep characteristics, and simultaneously to form Ca-Al compounds and Mg-Ca compounds, which are stable in a high-temperature region. These intermetallic compounds crystallize or precipitate mainly in crystalline grain boundaries in a network manner, and are accordingly believed to exert the wedge action of preventing the dislocation movement of magnesium alloys.

**【0013】** Due to the above-described reasons, the present magnesium alloy is believed to exhibit such good heat resistance that it undergoes the creep deformation less even in a high-temperature region when it comprises Al and Ca in an appropriate amount, respectively.

**【0014】** Next, the reasons why the present magnesium alloy is good in terms of the castability will be hereinafter described. Note that the "castability" referred to in the present specification designates whether cracks occur or not in casting. The cracks in casting can be classified as so-called hot cracks and shrinkage cracks. The hot cracks are cracks that occur when liquid-phase portions undergo volumetric contraction in the state of solid-liquid coexistence. Accordingly, dendritic structures or tree-like structures appear in fracture surfaces. On the other hand, the shrinkage cracks occur in the state free from liquid phases when being ruptured by casting residual stresses. Consequently, fracture surfaces are brittle fracture surfaces free from dendritic structures. Unless otherwise specified, both cracks are simply

referred to as casting cracks in the present specification without distinction. However, it is possible to say daringly that the hot cracks will be hereinafter considered primarily. This interpretation can be derived from the following fact. Since the hot cracks are affected greatly by the characteristics of magnesium alloys per se, it is difficult to solve the hot cracks by reviewing casting designs and production processes. On the contrarily, it is often possible to solve the shrinkage cracks by devising or elaborating mold configurations and casting methods. Indeed, the present magnesium alloy produces advantages not only in inhibiting the hot cracks but also in practically inhibiting the shrinkage cracks sufficiently. Hereinafter, the present magnesium alloy will be described with a focus on how it inhibits the casting cracks.

**【0015】** The present inventors first thought of narrowing the solidification temperature width of magnesium alloys in order to inhibit the casting cracks. The solidification temperature width is the temperature difference between the liquidus temperature at which molten metals start solidifying and the solidus temperature at which molten metals complete solidifying. When the solidification temperature width is narrowed, it is possible to effect advantages in inhibiting the casting cracks because the shrinkage stresses decrease when the molten metal of magnesium alloys solidifies. In order to narrow the solidification temperature width, it is required to increase the solidus temperature of magnesium alloys and to decrease the liquidus temperature.

**【0016】** According to the surveys and studies carried out by the present inventors, the solidus temperature of the present magnesium

alloy (e.g., an Mg-Ca-Al ternary alloy) is influenced strongly by Ca. Specifically, when Ca is contained less, the solidus temperature increases sharply to around 515 °C. When Al is added thereto, the solidus temperature increases in accordance with the Al addition, though the increment is gentle. For example, when the Ca content and the Al content are equivalent substantially like an Mg-3% by mass Ca-3% by mass Al alloy, namely, when the Al/Ca ratio by mass is 1 virtually, it was understood that the influence of Ca is predominant so that the solidus temperature is a temperature (e.g., about 515 °C) which is determined by the Mg-Ca binary phase diagram. Moreover, when the mass proportion of Al with respect to Ca, the Al/Ca ratio by mass, is 3 or more, the influence of Al is added moderately so that the solidus temperature increases to about 530 °C approximately. It is believed that Ca influences the solidus temperature strongly because the solidus temperature is constant substantially, at about 515 °C, in the Mg-Ca binary phase diagram when the Ca content falls in the claimed range according to the present invention.

**【0017】** On the other hand, regarding the liquidus temperature, Ca acts somewhat more strongly to lower the liquidus temperature than Al does, Ca and Al work cooperatively to influence the liquidus temperature as a whole. For example, an Mg-3% by mass Al-3% by mass Ca alloy exhibited a liquid temperature of 620 °C; an Mg-6% by mass Al-3% by mass Ca alloy exhibited a liquid temperature of 603 °C; and an Mg-3% by mass Al-9% by mass Ca alloy exhibited a liquid temperature of 581 °C.

**【0018】** From the facts, in order to narrow the solidification temperature width, it is important to have Ca contained in an amount

of 1% by mass or more so as to increase the solidus temperature to 515 °C or more; and to control the summed amount of Ca and Al to a predetermined amount or more so as to properly decrease the liquidus temperature. Since it is natural that the more the contents of Ca and Al increase the higher the solidus temperature increases but the lower the liquidus temperature decreases, it is preferable if only the solidification temperature width can be narrowed simply. However, when the contents of Ca and Al increase too much, it is not preferable economically because the cost of magnesium alloys has gone up. Moreover, when the content of Al increases too much with respect to the content of Ca, it is not preferable because it results in lowering the heat resistance of magnesium alloys as described above. In addition, when the content of Ca increases too much, there arise fears of lowering the molten metal flowability, fusing with molds and lowering the elongation.

**[0019]** In view of both heat resistance and castability, the contents of Ca and Al, the requisite elements, are controlled in the present heat-resistant magnesium alloy so that the content of Ca falls in a range of from 1 to 15% by mass, i.e., Ca: 1-15% by mass; and the summed content of Ca and Al falls in a range of from 4 to 25% by mass, i.e.,  $4\% \text{ by mass} \leq \text{Ca} + \text{Al} \leq 25\% \text{ by mass}$ . The composition can be interpreted as Ca: 1-15% by mass and Al: 3-10% by mass. The lower limit of the Ca content can preferably be 2% by mass, further 3% by mass; and the upper limit can preferably be 10% by mass, further 9% by mass. Moreover, the lower limit of the summed content of Ca and Al can preferably be 5% by mass, further 6% by mass, furthermore 9% by mass; and the upper limit can preferably be 20% by mass, further 18% by mass, furthermore 12% by mass. In addition, focusing on the

Al content specifically, the lower limit can preferably be 4% by mass, further 5% by mass; and the upper limit can preferably be 10% by mass, further 9% by mass.

**[0020]** When the content of Al is more than the content of Ca, it is not possible to sufficiently inhibit the  $Mg_{17}Al_{12}$  from precipitating so that the creep resistance of magnesium alloys is lowered as described above. Accordingly, it is preferred that the mass ratio of the Ca content with respect to the Al content, Ca/Al by mass, can be 1 or more, further 2 or more, furthermore 3 or more.

**[0021]** Since the present heat-resistant magnesium alloy has the above-described composition, it exhibits a solidification temperature width of 110 °C or less, further 100 °C or less, furthermore 90 °C or less, moreover 80 °C or less, still further 75 °C or less. When the solidification temperature width narrows as such, it means that the cooling rate enhances and the solidifying time shortens in all casting methods, contrary to the case where the cooling rate is simply increased in a specific casting method. Specifically speaking, the solidifying time shortens even in the gravity casting whose cooling rate is relatively slow, and shortens even more in the die-cast casting whose cooling rate is very fast. Since the solidifying time thus shortens, it is believed that the shrinkage stresses are suppressed in solidifying the molten metal so that the casting cracks are inhibited.

**[0022]** Moreover, when the present inventors observed the structure of cast products composed of the present heat-resistant magnesium alloy, it was verified that the structure was made finer remarkably. It is believed that the solidifying time shortened as described above is one of the causes of this phenomenon but the composition of the

present heat-resistant magnesium alloy as well affects the finer structure. The belief is because of the fact that the structure was not made finer so much when it contained R.E. even if the solidification temperature width was lowered to 80°C approximately. Therefore, making the structural roughness finer is believed to be effective in inhibiting the casting cracks. Since the structural roughness can be indexed with the average crystalline grain diameter, it is believed to be much more effective in order to inhibit the casting cracks when the average crystalline grain diameter is diminished more so as to be 18  $\mu\text{m}$  or less, further 16  $\mu\text{m}$  or less, furthermore 14  $\mu\text{m}$  or less, moreover 12  $\mu\text{m}$  or less, still further 10  $\mu\text{m}$  or less.

**【0023】** The present heat-resistant magnesium alloy can further comprise Mn. Mn is an element which solves into Mg crystalline grains to subject magnesium alloys to solid-solution strengthening. Moreover, Mn reacts with Al as well to inhibit  $\text{Mg}_{17}\text{Al}_{12}$ , one of the causes of lowering the creep strength or creep resistance, from precipitating and simultaneously form thermally stable intermetallic compounds. Due to the actions, Mn is an element which can improve not only the room-temperature strength of magnesium alloys but also the high-temperature strength. In addition, Mn does not adversely affect the castability of magnesium alloys. Besides, Mn produces an advantage of removing Fe, one of the impurities which cause corrosion, by sedimentation. When the present heat-resistant magnesium alloy comprises Mn too less, the advantages are effected less. When the present heat-resistant magnesium alloy comprises Mn in an amount of more than 1% by mass, not only the advantages cannot be expected to upgrade but also it is not economical. Hence,

it is appropriate that the present heat-resistance magnesium alloy can contain Mn in an amount of from 0.1 to 1% by mass, further from 0.2 to 0.7% by mass.

(Heat-resistant Magnesium Alloy Cast Product)

**【0024】** Not limited to the above-described present heat-resistance magnesium alloy for casting, it is possible to grasp the present invention as a cast product comprising the same. The cast product is made with the present heat-resistant magnesium alloy as a raw material.

**【0025】** For instance, a heat-resistant magnesium alloy cast product according the present invention is produced by a process comprising the steps of:

pouring a molten alloy into a mold, the molten alloy comprising:

Ca in an amount of from 1 to 15%;

Al in a summed amount of from 4 to 25% with the Ca amount; and

the balance being Mg and inevitable impurities when the entirety is taken as 100%; and

solidifying the molten alloy by cooling it after the pouring step.

**【0026】** The present heat-resistant magnesium alloy cast product is not limited to those made by the ordinary gravity casting or pressure casting, but can be those made by the die casting. Note that the terms, "for casting" and "castability" referred to in the present specification, are applicable to any casting method. Moreover, a mold used in casting does not matter whether it is sand molds or metallic molds.

**【0027】** In addition, the "heat resistance" set forth in the present specification is assessed by the mechanical qualities of magnesium alloys in a high-temperature atmosphere, for example, the creep characteristics or high-temperature strength which are examined by a stress relaxation test or an axial tension retention test.

**【0028】** In the present specification, when the composition range of the respective elements is specified in a form of "from x to y% by mass," it means to include the lower limit "x" and the upper limit "y" unless otherwise specified.

**【0029】** The application of the present heat-resistant magnesium alloy extends to various fields, such as automobiles and home electric appliances, starting with space, military and aeronautic fields. Indeed, it is more appropriate to use the present heat-resistant magnesium alloy for products used in high-temperature environments, such as engines, transmissions, air-conditioning compressors which are disposed in automotive engine rooms, or products related to them, by making the active use of the heat resistance.

#### BRIEF DESCRIPTION OF THE DRAWINGS

**【0030】** A more complete appreciation of the present invention and many of its advantages will be readily obtained as the same becomes better understood by reference to the following detailed description when considered in connection with the accompanying drawings and detailed specification, all of which forms a part of the disclosure:

Fig. 1 is a cross-sectional view for illustrating the shape of a mold;

Fig. 2 is metallic structure photographs which were obtained by observing the cross-section of test samples with a

metallographical microscope, wherein Fig. 2(a) is an image of the metallic structure of Test Sample No. 5 and Fig. 2(b) is an image of the metallic structure of Test Sample No. 7; and

Fig. 3 is a scatter diagram for illustrating the solidification temperature width and structural roughness of test samples as well as whether casting cracks occurred or not in the test samples.

#### DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

**【0031】** Having generally described the present invention, a further understanding can be obtained by reference to the specific preferred embodiments which are provided herein for the purpose of illustration only and not intended to limit the scope of the appended claims.

#### EXAMPLES

**【0032】** The present invention will be hereinafter described in detail with reference to specific examples.

**【0033】** A plurality of test samples were produced by changing the contents or addition amounts of Al, Ca and Mn in magnesium alloys variously. The resulting test samples were observed whether casting cracks occurred or not as well as for the structural roughness.

(Production of Test Samples)

**【0034】** A chloride flux was applied to the inner surface of a crucible. Note that the crucible was made of iron and was pre-heated in an electric furnace. A pure magnesium bare metal, pure Al and an Mg-Mn alloy were charged into the crucible, and were melted therein. Note that the raw alloy materials were weighed by a predetermined mass, respectively. Moreover, Ca weighed by a predetermined weight was

added to the resulting molten metal which was held at 750 °C (a molten metal preparing step).

**【0035】** The resultant molten metal was stirred fully to completely melt the raw materials. Thereafter, the molten metal was held still at the same temperature, 750 °C, for a while. While melting the raw materials, a mixture gas of a carbon dioxide gas and an SF<sub>6</sub> gas was sprayed onto the surface of the molten metal in order to inhibit Mg from burning, and the flux was spread on the surface of the molten metal whenever appropriate.

**【0036】** A variety of the thus produced molten alloys were poured into a mold which was formed as the configuration illustrated in Fig. 1 (a pouring step), and were solidified in air (a solidifying step). Thus, bottomed cylinder-shaped test samples (heat-resistant magnesium alloy cast products) were produced by the gravity casting. Note that the bottomed cylinder-shaped test samples had a bottom surface, whose thickness was about 3 mm and which was provided with a  $\phi$  17 mm opening, and had an outside diameter of about  $\phi$  60 mm. Table 1 below sets forth the chemical composition for every test sample.

(Observation on Casting Cracks and Structural Roughness

and

Solidification Temperature Width Calculation)

**【0037】** The resulting test samples were observed for the occurrence of casting cracks and the type of casting cracks visually and by means of a metallographical microscope. When dendritic structures were formed in the fracture surface of casting cracks, the casting cracks were considered the hot cracks; and when the fracture surface was brittle fracture surfaces, the casting cracks were considered

the shrinkage cracks. Table 1 sets forth the occurrence of casting cracks in the respective test samples together with the chemical compositions.

**[0038]** Moreover, the test samples were cut at the middle, and the structural roughness of the cut surface was observed by means of a metallographical microscope with 500 magnifications. Table 1 sets forth the results of the observation together with the other characteristics. Note that the structural roughness recited in Table 1 is an average structural roughness and is designated by an average crystalline grain diameter which was calculated from the average values of the size of  $\alpha$  phases in Mg. For reference, Figs. 2 (a) and 2 (a) depict the photographic image of the structure in Test Sample Nos. 5 and 7, respectively.

**[0039]** In addition, Table 1 sets forth the solidification temperature widths, which were calculated from the solidus temperature and liquidus temperature of the respective test samples, together with the above-described characteristics.

**[0040]** Fig. 3 summarizes the solidification temperature width, structural roughness and occurrence of casting cracks which were determined as described above.

TABLE 1

Test Sample No.	Chemical Composition (% by mass)						Casting Cracks	Structural Roughness ( $\mu\text{m}$ )	Liquidus Temp. ( $^{\circ}\text{C}$ )	Solidus Temp. ( $^{\circ}\text{C}$ )	Solidification Width ( $^{\circ}\text{C}$ )	Remarks
	Ca	Al	Mn	Zn	Sr	R.E.	Ca/Al					
1	3	6	-	-	-	-	0.5	None	14.8	604	530	74
2	3	9	-	-	-	-	0.3	None	15.5	598	530	68
3	13.5	4.5	-	-	-	-	3.0	None	7	545	515	30
4	3	3	0.2	-	-	-	1.0	None	11.8	620	515	105
5	9	3	0.5	-	-	-	3.0	None	11.4	580	515	65
6	9	3	0.7	-	-	-	3.0	None	11.8	585	515	65
7	13.5	4.5	0.2	-	-	-	3.0	None	7.2	545	515	30
C1	1	1	-	-	-	-	1.0	Hot Cracks	29.3	642	515	127
C2	4	-	-	-	-	-	-	Hot Cracks	1	629	515	114
C3	3	3	-	-	0.3	-	1.0	Hot Cracks	15	626	515	111
C4	3	1	-	-	3	-	3.0	Hot Cracks	23.5	628	515	105
C5	3	3	-	-	3	-	1.0	Hot Cracks	20.7	626	515	111
C6	1	6	-	-	3	0.2	0.2	Shrinkage Cracks	20	60	530	74
C7	1	9	-	-	3	0.1	0.1	Shrinkage Cracks	32.6	598	515	83
C8	1	6	-	0.5	-	3	0.2	Shrinkage Cracks	30.1	60	53	74
C9	2	5	0.3	-	-	2	0.4	Hot Cracks	25.2	617	530	87
C10	-	9	-	1	-	-	-	None	21.4	598	428	170

(Assessment)

**【0041】** The following are appreciated from Table 1 and Fig. 3.

**【0042】** (1) The compositions of Test Sample Nos. 1 through 7 fell in the claimed ranges according to the present invention. As a result, all of Test Sample Nos. 1 through 7 exhibited a solidification temperature width of 105 °C or less, and were made finer so that they exhibited a structural roughness of 16  $\mu\text{m}$  or less. Moreover, Test Sample Nos. 1 through 7 were little suffered from the occurrence of shrinkage cracks, not to mention hot cracks.

**【0043】** In addition, the more the Ca content was with respect to the Al content, namely, the larger the Ca/Al mass ratio was, Test Sample Nos. 1 through 7 exhibited a narrower solidification temperature width and simultaneously showed a finer structural roughness.

**【0044】** (2) The compositions of Test Sample Nos. C1 through C10 fell outside the claimed ranges according to the present invention. Except Test Sample No. C10, all of Test Sample Nos. C1 through C9 suffered from the occurrence of casting cracks. Note that it is believed that Test Sample No. C10 did not suffer from the occurrence of casting cracks because of the following fact. Since Test Sample No. C10 was made of an Mg-Al alloy whose heat resistance, especially creep resistance, was low inherently, it could deform easily by the stress in casting.

**【0045】** Test Sample Nos. C4 through C9 included "R.E." Accordingly, regardless of the solidification temperature width, all of Test Sample Nos. C4 through C9 exhibited a coarse structural roughness. Among Test Sample Nos. C4 through C9, test samples whose absolute Ca content was less and whose Al content was more with respect to

the Ca content, such as Test Sample Nos. C6 through C8, exhibited a coarse structural roughness, though they exhibited a narrow solidification width. Moreover, Test Sample Nos. C6 through C8 suffered from the occurrence of casting cracks. Note that all of the casting cracks were shrinkage cracks in Test Sample Nos. C6 through C8.

**[0046]** Having now fully described the present invention, it will be apparent to one of ordinary skill in the art that many changes and modifications can be made thereto without departing from the spirit or scope of the present invention as set forth herein including the appended claims.